

细梗香草的挥发油成分

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摘要 本文对报春花科植物细梗香草 (*Lysimachia capillipes* Hemsl.) 的挥发性成分, 用气相色谱和气质联用方法进行了定性和定量研究。鉴定出酸性成分75个, 中性成分74个。在中性成分中鉴定出六氢金合欢烯酰丙酮、苯乙醇及香叶基丙酮等; 酸性成分主要为棕榈酸、亚油酸、亚麻酸及一些二酸。

关键词 细梗香草; 挥发油; 棕榈酸; 六氢金合欢烯酰丙酮; 苯乙醇; 香叶基丙酮

细梗香草 (*Lysimachia capillipes* Hemsl.) 又名排草香、香排草、香草等, 为报春花科排草属植物, 产四川、湖北、云南、贵州、广东、福建等地。细梗香草性甘、味平; 全草入药, 治虚弱、感冒、咳喘、风湿痛及月经不调等症^[1]。细梗香草含挥发油且香气浓郁持久, 在香料工业中与灵香草一样, 均用于烟草香精中。关于灵香草 (*Lysimachia foenum-graecum* Hance) 的挥发油成分, 刘国声等曾报道过^[2-3]。但细梗香草的化学成分尚未见报道, 为了解其香味成分及利用价值, 我们对细梗香草的化学成分进行了研究。

实 验 部 分

提取分离 1公斤细梗香草用甲醇于室温浸泡三次, 抽提液经2%的活性炭脱色后, 减压回收至少许, 加水, 用乙醚萃取三次。乙醚液用5%碳酸氢钠溶液萃取四次。碱液用稀硫酸中和, 乙醚萃取, 得到酸性物质4.23克。该酸性成分按常法甲酯化得其甲酯3.63克。

碱处理后的醚层用水洗至中性, 溶剂回收后进行水蒸汽蒸馏, 得到黄色中性油0.75克。未蒸出部分用乙醚抽提得12.5克。该抽提物用硅胶进行柱层析, 溶剂用、石油醚-丙酮10:1、5:1、5:2及1:1, 丙酮洗脱, 得到化合物A、B及其余四个微量成分。其中化合物A得6.22克。经质谱和红外光谱鉴定, A为棕榈酸, B为豆甾醇。

中性油和酸性成分的甲酯分别进行气相色谱和色谱-质谱分析。

气相色谱 岛津GC-9A; 数据处理为C-R 3A; SE-54石英毛细管柱, 30m×0.25mm

(美国J&W公司), 柱温80—200℃, 程序升温3℃/min, 进样温度230℃, 检测器FID。

气相色谱-质谱 仪器为Finnigan 4510 GC/MS/DS; 色谱条件同上; EI, 电子能量70eV; 灯丝电流0.25mA; 倍增器电压1200V。数据处理使用INCOS系统。各分离组分首先通过NIH/EPA/MSDB计算机谱库(美国国家标准局NBB LIBRARY谱库)进行检索, 并参照有关文献^[4]对各质谱图进行解析来确认。

化合物A用石油醚重结晶得白色针晶, mp 57.5—59℃。经红外光谱和质谱鉴定, 并与标准品对照, 为棕榈酸。

化合物B用甲醇重结晶得白色针晶, mp 163—165℃。经红外光谱和质谱鉴定, 并与标准品对照, 为豆甾醇。

结果与讨论

细梗香草挥发性成分主要为酸类及中性成分。在我们鉴定的75个酸性成分中(表1), 有不同链长的饱和酸、不饱和酸以及芳香酸、二羧酸等, 其中以棕榈酸含量最高, 其次为亚油酸、亚麻酸等。在中性成分中鉴定出74个化合物(表2), 其中有植物中较少见的六氢金合欢烯酰丙酮。此外, 含有苯乙醇、香叶基丙酮等。

从我们的分析结果看, 细梗香草的特征香气, 主要由有机酸及挥发油提供。从挥发性物质的含量及种类来看, 细梗香草较灵香草在香料工业上更有价值。

表1 细梗香草中的酸性成分

Table 1 The acidic constituents in *Lysimachia capillipes* Hemsl.*

No.	Compounds	Retation** time (mins)	Content (%)	No.	Compounds	Retation time (mins)	Content (%)
1	2-methylbutanoic acid	3.11	1.05	12	E-4-heptenoic acid	6.93	0.03
2	Valeric acid	3.51	0.05	13	enanthic acid	7.03	0.32
3	2-methylene butanoic acid	4.03	0.08	14	succinic acid	7.83	0.04
4	3-methylvaleric acid	4.23	0.05	15	methylsuccinic acid	8.12	0.03
5	caproic acid	4.85	1.20	16	E-2-heptenoic acid	8.35	0.06
6	3-hexenoic acid	4.99	0.16	17	benzoic acid	9.33	0.60
7	E-2-hexenoic acid	5.69	0.11	18	3-octylenic acid	9.79	0.19
8	furancarboxylic acid	5.92	0.06	19	caprylic acid	10.09	0.73
9	2-hydroxy-4-methylvaleric acid	6.21	0.10	20	β -hydroxyvaleric acid	10.47	0.24
10	2-hydroxy-3-methylvaleric acid	6.33	0.56	21	2-octylenic acid	11.78	0.15
11	6-heptenoic acid	6.80	0.01	22	phenylacetic acid	12.19	0.75

(续表 1)

23	2,2-dimethylglutaric acid	12.68	0.05	52	tetradecenic acid	33.23	0.32
24	3-methylbenzoic acid	13.39	tr.	53	myristic acid	34.06	0.57
25	6-nonenoic acid	13.53	0.04	54	3,4-dihydroxybenzoic acid	34.34	0.09
26	pelargonic acid	13.83	0.57	55	undecandioic acid	35.05	0.47
27	malic acid	15.08	0.03	56	trans-cinnamic acid	35.93	0.25
28	2,6-nonadienoic acid	15.40	0.14	57	pentadecenoic acid	36.38	1.80
29	2-nonenoic acid	15.75	0.09	58	pentadecanoic acid	37.70	0.22
30	phenylpropionic acid	16.28	0.01	59	2-hydroxytetradecanoic acid	38.33	1.01
31	decylenic acid	17.60	0.17	60	4-acetyloxy--3methoxycin- namic acid	38.66	0.15
32	capric acid	17.93	0.43	61	dodecandioic acid	39.03	0.16
33	pimelic acid	19.29	0.04	62	3-hydroxytetradecanoic acid	39.16	0.30
34	2-hydroxy-3-methylbenzoic acid	19.50	0.16	63	14-methylpentadecanoic acid	39.65	0.14
35	4-oxononanoic acid	19.96	0.36	64	11-hexadecenoic acid	40.47	0.81
36	α -hydroxyphenylpropionic acid	20.31	0.15	65	palmitic acid	41.46	18.62
37	cinnamic acid	20.69	0.11	66	15-methylhexadecanoic acid	43.86	2.04
38	10-undecenoic acid	21.45	0.11	67	14-methylhexadecanoic acid	44.41	0.55
39	undecenoic acid	21.80	0.07	68	heptadecenoic acid	44.67	0.32
40	undecoic acid	22.13	0.13	69	margaric acid	45.57	0.60
41	suberic acid	23.19	0.27	70	2-hydroxyhexadecanoic acid	46.18	0.74
42	3-hydroxybenzoic acid	24.36	0.45	71	linoleic acid	49.68	14.81
43	4-hydroxyphenylacetic acid	25.41	3.69	72	linolenic acid	50.11	14.66
44	lauric acid	25.85	0.71	73	oleic acid	51.08	1.20
45	vanillic acid	26.30	2.77	74	stearic acid	51.63	3.08
46	azelaic acid	27.38	3.24	75	nonadecanoic acid	58.30	0.40
47	4-acetyloxy-3-methoxyben- zoic acid	28.88	0.21				
48	tridecenoic acid	29.50	0.04				
49	tridecanoic acid	30.26	0.23				
50	sebacic acid	31.29	0.36				
51	p-hydroxycinnamic acid	32.16	0.18				

* 酸性成分均以其甲酯形式鉴定。 ** 保留时间为其酸甲酯的保留时间

* The acidic constituents were identified in the form of their methyl esters. ** The retention time are the retention time of methyl ester of their acids

表2 细梗香草精油化学成分

Table 2 The chemical constituents in essential oil of *Lysimachia capillipes* Hemsl.

No.	Compounds	Retation time (mins)	Content (%)	No.	Compounds	Retation time (mins)	Content (%)
1	furfural	3.15	0.13	31	verbenone	13.40	0.28
2	n-hexanol	4.10	0.06	32	2-ethyl-4-methylphenol	14.98	0.46
3	2-hydroxymethyl tetrahydropyran	4.48	0.12	33	2,4-dihydroxyacetophenone	15.67	1.89
4	methyl 3-methylvalerate	4.72	0.04	34	lauraldehyde	16.68	0.18
5	hydroperoxide, pentyl	4.81	tr	35	1,2,3-trimethoxybenzene	17.03	0.70
6	hydroperoxide, 1-methylhexyl	4.93	0.08	36	methyl caprate	17.38	0.82
7	2-ethyl-4-pentenal	5.28	0.14	37	3-methoxy-2,5,6-trimethyl- phenol	17.63	0.11
8	5-methylfurfural	5.48	0.12	38	3,4-dimethoxyphenol	18.72	2.44
9	methyl 3-methyl-2-oxovalerate	5.67	0.50	39	2-methyl-1,4-benzenedicar- boxaldehyde	18.92	0.29
10	phenol	5.78	1.94	40	eugenol	19.08	0.04
11	6-methyl-5-hepten-2-one	6.07	0.61	41	γ -nonalactone	19.20	0.38
12	2-pentylfuran	6.33	0.13	42	2-methoxy-4-propylphenol	19.31	0.10
13	methyl 2-hydroxy-3-methyl- valerate	6.57	0.04	43	veratric acid	20.80	0.84
14	2,6-dimethyl-4-heptanol	7.03	0.13	44	γ -ionone	21.98	0.31
15	benzyl alcohol	7.30	0.57	45	geranylacetone	22.75	2.71
16	o-cresol	7.65	1.39	46	3,5-dimethoxy-4-hydrox- yacetophenone	23.95	0.58
17	m-cresol	8.28	2.13	47	β -ionone	24.20	0.59
18	o-methoxyphenol	8.73	0.88	48	2,6-dilert-,butyl-4-methyl- phenol	25.33	0.21
19	linalool	8.93	0.50	49	methyl laurate	25.63	1.59
20	6-methyl-3,5-heptadien-2-one	9.10	0.45	50	2,6-dihydroxy-4-methox- yacetophenone	25.90	1.52
21	phenylethyl alcohol	9.62	6.54	51	3-(2-pentenyl)-1,2,4- cyclopentanetrione	26.20	3.12
22	3,5,5-trimethyl-2-cyclohexen-1- one	9.85	0.76	52	8-hydroxy-3-methylisocou- marin	26.72	0.71
23	phlorol	10.35	0.04	53	ψ -ionone	27.97	0.19
24	1,2-dimethoxybenzene	10.52	0.41	54	2,4-dimethoxy-1-phenyl acetone	28.15	0.24
25	2,3-dimethylphenol	10.70	0.78	55	2,6-dimethoxy-4-allylphenol	28.93	0.12
26	p-ethylphenol	11.38	1.73				
27	isoborneol	11.70	0.63				
28	4-ethyl-1,3-benzenediol	12.30	0.90				
29	safranal	12.60	0.21				
30	1,4-dimethyl-2-isobutylcyclo- hexane	12.98	0.10				

(续表 2)

56	diphenylacetaldehyde	29.17	0.25	65	nonadecanol	38.32	0.14
57	methyl tridecanoate	29.55	0.12	66	methyl palmitate	40.55	10.18
58	δ -cadinol	30.08	0.19	67	dibutyl phthalate	41.13	0.22
59	2,4-dihydroxy-6-methyl-1,3 benzenedicarboxaldehyde	31.22	1.03	68	methyl 15-methylhexadeca- noate	42.85	0.77
60	methyl myristate	33.35	0.40	69	methyl heptadecanoate	43.71	0.12
61	phenanthrene	3.542	0.08	70	methyl linoleate	48.08	6.94
62	methyl pentadecanoate	36.95	0.33	71	methyl linolenate	48.47	5.83
63	3,4,4a,5,6,7-hexahydro-1,1, 4a-trimethylnaphthalenone	37.34	0.04	72	methyl oleate	48.68	0.44
64	hexahydrofarnesyl acetone	37.67	1.71	73	phytol	49.10	0.95
				74	methyl stearate	49.93	0.83

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THE VOLATILE CONSTITUENTS OF *LYSIMACHIA CAPILLIPES*

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Abstract The volatile constituents of *Lysimachia capillipes* Hemsl. were studied by means of GC & GC/MS/DS. 75 acidic and 74 neutral constituents were identified qualitatively and quantitatively. Hexahydrofarnesylacetone, phenylethyl alcohol and geranylacetone were identified in the neutral constituents. The main components of acidic constituents are palmitic acid, linoleic acid, linolenic acid and some diacids. The acidic and neutral constituents form the peculiar flavor of *Lysimachia capillipes*.

Key words *Lysimachia capillipes*; Volatile oil; Palmitic acid; Hexahydrofarnesylacetone; Phenylethyl alcohol; Geranylacetone